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The pyrolytic-plasma method and the device for the utilization of hazardous waste containing organic compounds

Teresa Opalińska[a], Bartłomiej Wnęk[a,*], Artur Witowski[a], Rafał Juszczuk[a], Małgorzata Majdak[a], Stanilav Bartusek[b]

[a] Tele and Radio Research Institute, Ratuszowa 11, 03-450 Warsaw, Poland
[b] VŠB—Technical University of Ostrava, 17. listopadu 15/2172, 708 33 Ostrava – Poruba Czech Republic

HIGHLIGHTS

- A first stage of the process of waste utilization consisted in pyrolysis of waste.
- Then the pyrolytic gas was oxidized with a use of non-equilibrium plasma.
- The device for the process implementation was built and characterized.
- Correctness of the device operation was proven with a use of the decomposition of PE.
- Usefulness of the method was proven in the process of utilization of EW.

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ABSTRACT

This paper is focused on the new method of waste processing. The waste, including hazardous waste, contain organic compounds. The method consists in two main processes: the pyrolysis of waste and the oxidation of the pyrolytic gas with a use of non-equilibrium plasma. The practical implementation of the method requires the design, construction and testing of the new device in large laboratory scale. The experiments were carried out for the two kinds of waste: polyethylene as a model waste and the electronic waste as a real waste. The process of polyethylene decomposition showed that the operation of the device is correct because 99.74% of carbon moles contained in the PE samples was detected in the gas after the process. Thus, the PE samples practically were pyrolyzed completely to hydrocarbons, which were completely oxidized in the plasma reactor. It turned out that the device is useful for decomposition of the electronic waste. The conditions in the plasma reactor during the oxidation process of the pyrolysis products did not promote the formation of PCDD/Fs despite the presence of the oxidizing conditions. An important parameter determining the efficiency of the oxidation of the pyrolysis products is gas temperature in the plasma reactor.

1. Introduction

Waste is an integral part of our civilization. In today's society, the human population tends to produce a large amount of waste on yearly basis, including household and industrial waste. These waste products are likely to take up our entire living space and completely pollute the environment, in the nearby future. Additionally, this would be a terrible mismanagement, because waste can be processed into energy and furthermore it can be treated as a source of obtaining and/or recovering valuable raw materials [1–8]. This is perhaps increasingly important nowadays, as we are more aware of the depletion of natural sources of raw materials, especially the hydrocarbon fuels.

According to the European Parliament and Council Directive 2008/98/EC of 19 November 2008 [9] waste is defined as "any substance or object which the holder discards or intends or is required to discard". Directive 2008/98/EC determines the order of priority for legislation and policy concerning waste prevention and waste management. The most important aim of waste management is to prevent it's formation. However, when the waste has already been unavoidably produced, we should firstly consider re-using it. If this is not possible, the waste should be recycled and then prepared for other methods of resource recovery, for example energy pro-

* Corresponding author.
E-mail address: bartlomiej.wnek@itr.org.pl (B. Wnęk).

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duction. At the very end of the waste management hierarchy is the disposal.

The problem that requires a solution, is finding an appropriate way of waste processing. Table 1 shows the percentage share of used methods of waste treatment in most of the European countries and in Turkey according to data for 2012 [10]. In Poland, 25.3% of waste was deposited into landfills on the ground and below it, contrasting with the Netherlands and Belgium where only 3.3% and 7.6%, of waste was disposed into landfill sites respectively. In Bulgaria and Romania, more than 90% of the waste was stored in this way. Processing of waste by recovery (other than the energy recovery and excluding storage in the excavations) was the highest in Belgium (73.2%) and the lowest in Iceland (1.0%). In Iceland, up to 67,4% of produced waste was incinerated, also with the energy recovery. In Poland, only 2.2% of generated waste was incinerated, 21.8% was stored in excavations and 50.4% was recovered in a different way (other than storing in the excavations and the energy recovery). The definition of the term "recovery" is given in Directive 2008/98/EC [9]. The recovery means "any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy". The quoted statistics show a significant area for improvement in Poland in regards to waste recovery and disposal.

The extremely diverse characteristics of waste, including hazardous waste and a wide range of possible applications, mean that a universal method of waste processing does not exist. Hence the aim of the following work was to design, construct and test a modular large laboratory scale device in order to study the processing of waste; including hazardous waste containing organic components. This new idea of waste processing consisted of a combination of two processes: 1—the pyrolysis of waste and 2—the oxidation of the pyrolytic gas with a use of non-equilibrium plasma. Therefore, the experimental research focused on the results obtained from both of the processes.

2. Experimental

2.1. Modular large scale laboratory device for waste utilization (MLDWU)

In the design of the device for the waste disposal and/or utilization it is assumed that: 1—the waste will contain organic components which can be processed by the pyrolysis process, 2—pyrolysis will be carried out in an inert gas atmosphere in order to reduce the probability of formation of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), 3—hydrocarbons which will form a component of the gases after the thermal decomposition of waste will be oxidized with the use of pure oxygen instead of oxygen from the air in order to avoid the formation of NO_x, 4—gases after the oxidation will be cooled and cleaned of dust, acidic and other harmful components including the PCDD and PCDF, and 5—the device will be constructed on a large laboratory scale.

MLDWU consisted of five modules: 1—a module of a pyrolytic reactor; 2—a module of a plasma reactor; 3—a module of a heat exchanger; 4—a module of a catalytic reactor, and 5—a module a neutralizer/adsorber (Fig. 1).

The module of the pyrolytic reactor consisted of the pyrolytic reactor and the feeder of solid waste. The pyrolytic reactor consisted of: 1—pyrolysis chamber in the form of a cylinder made of heat-resistant steel; it was closed by flap, 2—an electric heater, 3—argon feeding system and 4—system for protection against breakdown. The pyrolysis of waste was carried out in the inert gas (argon) atmosphere (Ar_I). The working gas, the heated argon was introduced into the pyrolytic chamber from the bottom and flowed upwards through the chamber. The feeder worked in the flow of argon (Ar_{II}). The process of pyrolysis was carried out in isothermal conditions. In the pyrolytic reactor the pressure (p) and the temperature of pyrolysis were measured. The pyrolytic gas containing argon and hydrocarbons. During the pyrolysis of a single waste sample, the momentary total concentration of hydrocarbons in the pyrolytic gas (C_Σ) should reach a maximum. At the time corresponding to the maximum of hydrocarbon concentration in the pyrolytic chamber, the maximum momentary pressure (p) should be reached (Fig. 1).

Subsequently, the pyrolytic gas were oxidized with the use of oxygen in the module of plasma reactor. The module of plasma reactor consisted of: 1—the plasma reactor, operating on the principle of gliding discharge, 2—the electric power supply essential for generating the discharge, and 3—the measuring systems enabling the measure of: the flow of oxygen and reactor cooling water, temperature of the gas in the reactor and the power supplied to the reactor. The plasma reactor was built with a steel tube closed on one side with disk, in which three knife-shaped electrodes, an ignition electrode and a set of special nozzles introducing gases into the reactor were located. The total gas flow through the plasma reactor amounted to between 3.00–10.0 Nm^3/h. These gases consisted of oxygen and the mixture of pyrolytic gas and argon. The gases leaving the module of the pyrolytic reactor and the oxygen were introduced into the plasma reactor separately and were mixed just before the discharge zone. The temperature of the gas in the plasma reactor was measured in the axis of the reactor outside the discharge zone at distance of about 50 mm from the gas outlet from the plasma reactor. The plasma reactor was supplied with high-voltage sinusoidal alternating current with 50 Hz of frequency. The plasma generated in gliding discharge was a non-equilibrium plasma that is characterized by high temperature of the inert gas (up to 2500 K depending on the discharge power) and the presence of high energy electrons (1 eV) [11]. In such conditions, chemical reactions are initiated not only by collisions of molecules of gas or vapour with electrons, but also by high temperature. The components of the pyrolytic gas introduced into gliding discharge with oxygen were decomposed and oxidized. The power (P) supplied to the plasma reactor depends on the qualitative and quantitative composition of the pyrolytic gas. It reaches a minimum at the time corresponding to the maximum of momentary temperature measured at the end of the plasma reactor (t) (Fig. 1)

The plasma reactor is a universal device. It can be used not only for the full oxidation of hydrocarbons, but also in the same reactor, a so called "syngas" (a mixture of carbon monoxide and hydrogen) or short-chain aliphatic hydrocarbons and/or carbon black can be obtained [12–19]. The combustion of these compounds can recover energy. This is one of the ways of the waste utilization. As a result, the waste utilization can be carried out in various ways in the same device by changing only the conditions of process. It can also be expected that different conditions (from the conventional combustion reaction) in the plasma reactor will not promote the formation of polynuclear/polycyclic aromatic compounds and their derivatives [20–24]. Consequently, a low concentration of PCDDs and PCDFs in the exhaust gases emitted from the utilization process of waste containing chlorine is expected [25,26].

In the module of heat exchanger, the gases after the oxidation reaction were cooled. The module of heat exchanger consisted of: 1—a shell-and-tube heat exchanger cooled by water 2—a vessel for the condensed water vapour and 3—connecting pipe to sampling the post-reaction gas. The measurement of the volume of post-reaction gas and its temperature was performed after the heat exchanger.

Table 1
The percentage share of different ways of waste treatment in EU countries and in Iceland and Norway.

Country	Deposit onto or into land	Land treatment and release into water bodies	Incineration/disposal	Incineration/energy recovery	Recovery other than energy recovery—backfilling	Recovery other than energy recovery—except backfilling
European Union (28 countries)	41.1	6.1	1.7	4.4	9.4	37.3
Belgium	7.6	0.0	8.1	11.2	0.0	73.2
Bulgaria	98.6	0.1	0.0	0.1	0.0	1.1
Czech Republic	19.9	0.2	0.4	5.3	28.1	46.1
Denmark	16.1	0.0	0.0	24.2	0.0	59.7
Germany	18.0	0.0	3.1	9.6	25.9	43.3
Estonia	39.6	0.0	0.0	1.7	20.4	38.3
Ireland	40.1	22.0	0.5	1.8	21.9	13.7
Greece	85.4	2.7	0.0	0.2	7.6	4.1
Spain	44.1	0.4	0.0	3.0	7.6	44.9
France	33.0	0.3	2.3	3.7	12.6	48.2
Croatia	63.9	0.2	0.0	1.3	1.4	33.2
Italy	20.2	0.0	4.8	1.9	0.3	72.9
Cyprus	68.8	0.0	0.3	0.1	11.1	19.7
Latvia	35.8	3.1	0.1	9.7	0.0	51.3
Lithuania	72.1	2.0	0.0	2.4	0.0	23.4
Luxembourg	34.0	0.0	1.3	0.4	18.8	45.5
Hungary	52.8	0.0	0.7	7.4	3.4	35.8
Malta	49.2	38.4	0.4	0.0	3.4	8.6
Netherlands	3.3	36.3	1.3	7.5	0.0	51.5
Austria	36.3	0.0	0.2	10.3	8.7	44.4
Poland	25.3	0.1	0.2	2.2	21.8	50.4
Portugal	37.1	0.0	0.7	17.0	0.0	45.1
Romania	90.5	0.9	0.0	0.7	0.0	7.8
Slovenia	12.6	0.0	0.7	6.4	21.7	58.5
Slovakia	54.7	1.8	1.0	3.8	0.0	38.7
Finland	52.8	0.2	0.5	11.4	0.0	35.0
Sweden	51.7	31.0	0.0	4.4	0.5	12.4
United Kingdom	24.1	19.2	3.7	0.2	7.1	45.7
Iceland	29.1	0.0	2.5	67.4	0.0	1.0
Norway	12.9	0.0	0.9	42.3	1.4	42.6

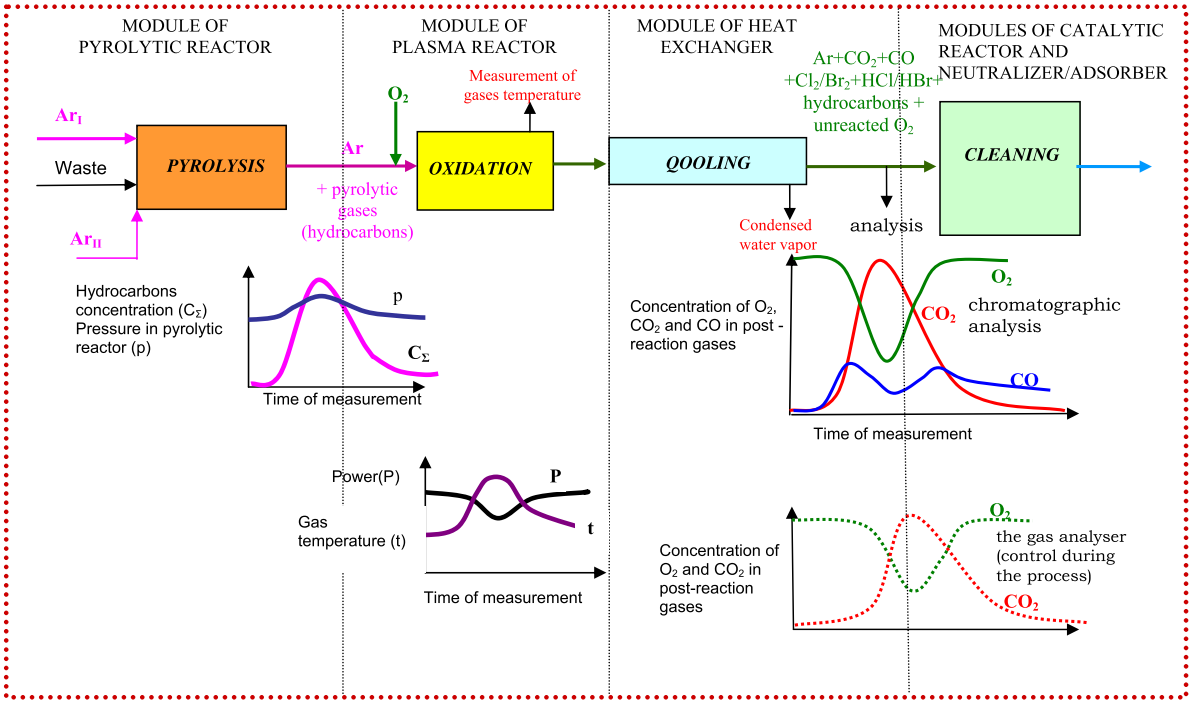

Fig. 1. The principle of the operation of the modular device for studying the process of waste utilization (explanation in the text).

The module of catalytic reactor was used for decomposition of PCDDs and PCDFs contained in the post-reaction gas. It consisted of: 1—a proper catalytic reactor 2—a heat exchanger and 3—a water cooler. The catalytic reactor was filled with catalyst that degrades, PCDD, PCDF, chlorophenols and chlorobenzenes. The catalyst also degrades hydrocarbons containing bromine in their molecular structure. The optimal temperature range of working catalyst was 300–350 °C. The module of catalytic reactor was used only when the waste containing chlorine and/or bromine in elemental composition was processed.

Table 2
Elemental composition and calorific value of electronic waste and residue after pyrolysis of electronic waste (pyrolysis temperature 600 °C).

Parameter	Unit	EW	Residue after pyrolysis of EW
Content of combustible parts	%	40,38	10,95
Content of volatile matter	% c.p.	80,21	13,79
Heat of combustion	kJ/kg	12327	3591
Calorific value	kJ/kg	11966	3591
Elemental analysis of combustible part			
C	% c.p.	65,73	71,05
H	% c.p.	4,11	0
S	% c.p.	0	0
N	% c.p.	0,02	0,05
Cl	% c.p.	1,49	0,15
O	% cz.p.	28,65	17,84

The module of neutralizer/adsorber consisted of a neutralizer and an adsorber. The active substance in the neutralizer was NaOH mounted on γ-Al2O3 and the activated carbon was the active substance in the adsorber.

2.2. Experiments

In the experiments a model waste and a real waste were used. Polyethylene (PE) with low density Malen E FGAN, 18-D008 manufactured by Basell Orlen Polyolefins Sp. z o.o of the granules having a diameter of 3.5–4.5 mm was the model waste. The waste was characterized by a high calorific value (approx. 50 MJ/kg). The bulk density of polyethylene amounted to 910–930 kg/m^3.

The real waste was the electronic waste (EW)—printed circuit boards without electronic and metal components, shredded into pieces of a diameter amounted to about 5 mm. The calorific value of EW was 11.97 MJ/kg. The real waste contained 40.38% wt. of combustible part, which contained 80.21% wt. of volatiles. Elemental analysis of combustible part showed 65.73% wt. of C, 4.11% wt. of H, 0.02% wt. of N, 1.49% wt. of Cl, and 28.65% wt. of O (Table 2). The thermal properties of the waste were characterized by DSC-TGA curves (Fig. 2). They were made with a use of simultaneous thermal analyzer SDT Q600 TA Instruments. The measurement was performed in argon at a flow rate of 100 ml/min. The weight of the sample changed as the temperature increased, which shows that the waste does not have a homogeneous composition. The largest loss in weight of the sample was observed in the temperature range 300–400 °C. In this temperature range two main groups of components of the waste were decomposed. Further increase of the temperature led to another, but lower loss of weight. Therefore, the temperature in the pyrolytic reactor was set at 600 °C to ensure total decomposition of the waste to vapour and gas during the pyrolysis process.

The experimental parameters are shown in Table 3. The total flow of gases introduced into the plasma reactor (without hydrocarbons produced during the pyrolysis of the waste) were similar for both experiments and amounted to 5.18 Nm^3/h for decomposition of PE and 5.20 Nm^3/h for decomposition of EW. All the gas flows are referenced to a temperature value of 273.14 K and a pressure value of 1013.25 hPa. During the processing of 25 g PE samples, additional, complementary argon was introduced into the plasma reactor in order to improve the work of the system introducing gas into the plasma reactor.

The post-reaction gas was sampled at predetermined time intervals. Qualitative and quantitative analysis of the post-reaction gas was performed with a use of gas chromatography. Gas chromatographs Shimadzu 2014 equipped with TCD and FID detectors were applied. The inorganic components of the post-reaction gas (H_2, O_2, CO and CO_2) were analyzed with a use of a packed column with a stationary phase Carboxen-1000 (5 ft x 1/8"SS; 40/60 mesh) manufactured by Supelco. The organic components of the post-reaction gas (C_1–C_4) were analyzed with a use of wide bore column GS—CARBONPLOT (30 × 0.533 mm × 3.00 μm) J & W GC Columns. The reference mixtures of gases by Air Liquide and Messer companies were used to calibrate the columns.

3. Results and discussion

3.1. Utilization of PE

The first stage in the utilization process of 25 g PE sample was the pyrolysis in argon in the pyrolytic reactor. The moment at which a single waste sample was introduced into the pyrolytic reactor corresponds to the time measurement of zero. It took about one minute, from the point at which a single waste sample was introduced into the pyrolytic reactor, until the entire portion of the sample was put in the pyrolytic reactor. During this one minute interval the pyrolysis of PE started. The momentary total

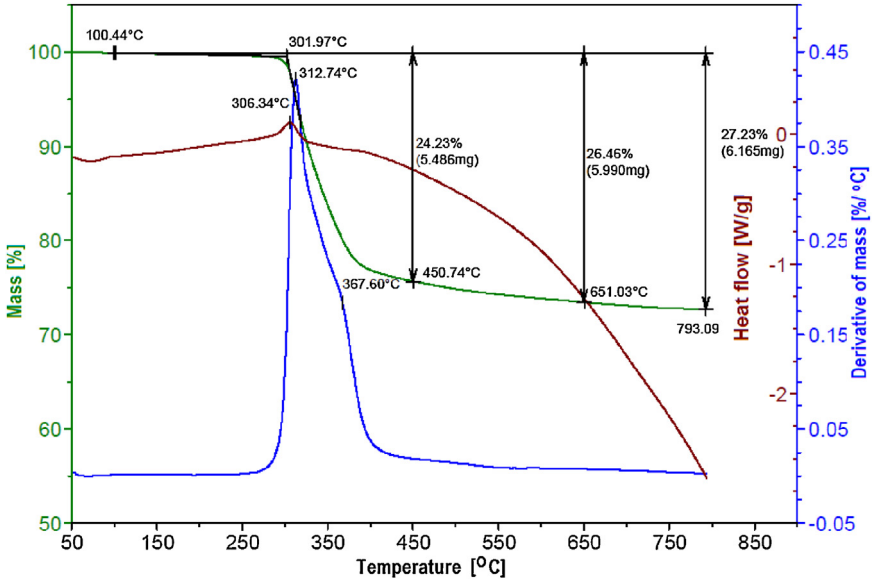

Fig. 2. Characteristics of thermal properties of the electronic waste (EW). TGA-DSC curves.

Table 3
The experimental parameters.

Type of waste	Polyethylene (PE)	Electronic waste (EW)
Mass of samples [g]	25	150
Argon flow through the pyrolytic reactor (A_{rI}) [Nm3/h]	1.20	1.60
Argon flow through the feeder of waste (A_{rII}) [Nm3/h]	0.30	0.40
Argon complementary introduced into the plasma reactor [Nm3/h]	0.48	–
Oxygen introduced into the plasma reactor (V_{oxygen}) [Nm3/h]	3.20	3.20
Residence time of argon in the pyrolytic reactor (τ) [s]	72	54
Minimal power in the plasma reactor [kW]	2.15	2.10
Temperature in the pyrolytic reactor [°C]	600	600
Number of samples	3	3

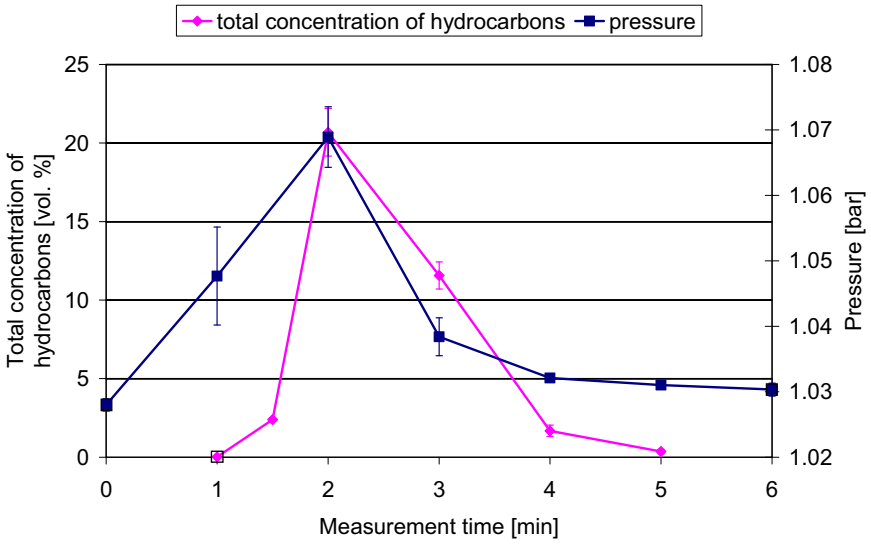

Fig. 3. The momentary total concentration of hydrocarbons C_1–C_4 (C_Σ) in the pyrolytic gas introducing from the pyrolytic reactor into the plasma reactor and the momentary pressure in the pyrolytic reactor during the thermal decomposition of the 25 g PE samples (data from the gas chromatography).

concentration of hydrocarbons produced during the pyrolysis varied in time (Fig. 3). The maximum value of total concentration of aliphatic hydrocarbons C_1–C_4 (C_Σ) leaving the pyrolytic reactor corresponded to the maximum of momentary pressure in the pyrolytic reactor (p) (Fig. 3).

Before turning on the electrical discharge, only the hot stream of argon, with temperature equaling to temperature of pyrolysis (600 °C) was introduced into the plasma reactor. Inside the plasma reactor the hot stream of argon was cooled to the temperature equal to several dozen of degrees (39 °C). Turning on the electrical discharge caused the increase of argon temperature in the plasma reactor, reaching up to 195 °C. Starting the oxidation process of the pyrolytic gas resulted in further increase of the gas temperature in the plasma reactor. Thus, the increase of gas temperature was caused by two factors: 1—the generation of the electrical discharge and 2—the course of the exothermic reaction. After one minute of the oxidation process, the momentary gas temperature amounted to 350 °C. The plasma oxidation of the pyrolytic gas with the highest momentary total concentration of hydrocarbons caused the increase of gas temperature up to 550 °C (Figs. 3 and 4).

The course of the momentary value of aliphatic hydrocarbon's total concentration in the pyrolytic gas before introducing it into the plasma reactor, and the temperature course of the gas in the plasma reactor after the oxidation of the pyrolytic gas (Figs. 3 and 4) indicated that the pyrolytic gas should contain, especially in the initial phase of the pyrolysis, not only aliphatic hydrocarbons C_1–C_4, but also hydrocarbons with more atoms of. It was indicated by the significant increase of the momentary temperature of the gas in the plasma reactor in reference to the C_Σ value in the first minute of the oxidation process. This conclusion was supported by the analysis of the composition of the pyrolytic gas performed using the method of mass spectroscopy thermobalance coupled with mass spectroscope. During the thermal decomposition of the sample were hydrocarbons C_1–C_4.

The hydrocarbons contained in the pyrolytic gas had a dual function in the oxidation process. On one hand they were substrates of the chemical reaction, and on the other hand they were the fuel determining the raise of the gas temperature in the plasma reactor. There was a feedback between the concentration of hydrocarbons in the pyrolytic gas and the observed gas temperature in the oxidation process in the plasma reactor. For used of electric supplier to the plasma reactor, the discharge power depended on (for given flows of oxygen and argon) the momentary concentration of hydrocarbon in the pyrolytic gas introduced into the plasma reactor (Figs. 3 and 4).

The samples of the post-reaction gas were collected for the analysis every 0.5 min, starting from the first minute of the experiment (from the moment of starting the introduction of the waste sample from the feeder of the solid waste into the pyrolytic reactor). From the first minute of the experiment the momentary CO_2 concentration was increasing and reached the maximum value after two minutes from the start of the experiment (Fig. 5). The maximum of the momentary CO_2 concentration corresponded to the minimum of the momentary O_2 concentration. At the time, for which the CO_2 concentration reached maximum, no CO was detected using the applied analytical method (Table 4). At this point of the oxidation process, the hydrocarbon's oxidation was the most efficient.

The momentary CO_2 concentration in the gas after the oxidation process of pyrolytic gas in the plasma reactor was closely associated with the momentary total concentration of hydrocarbons in

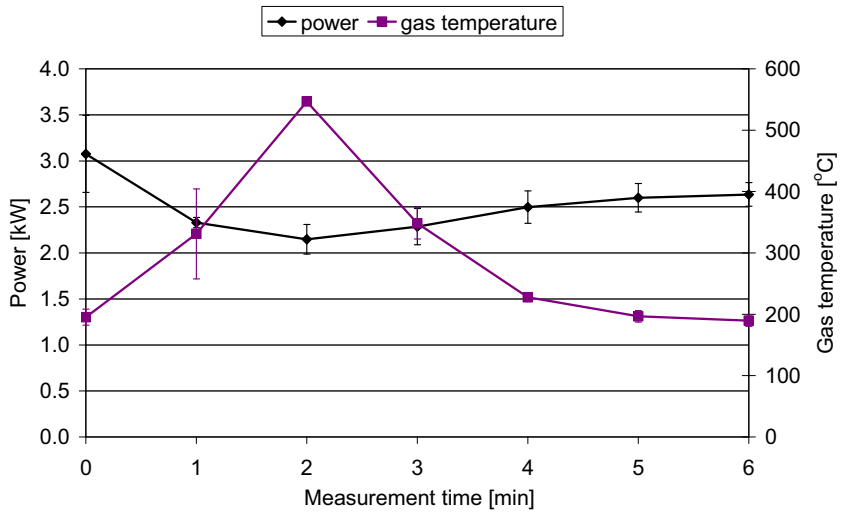

Fig. 4. The course of curve of power supplied to the plasma reactor and the course of curve of the gas temperature at the end of the plasma reactor during the 25 g PE samples utilization (explanation in the text).

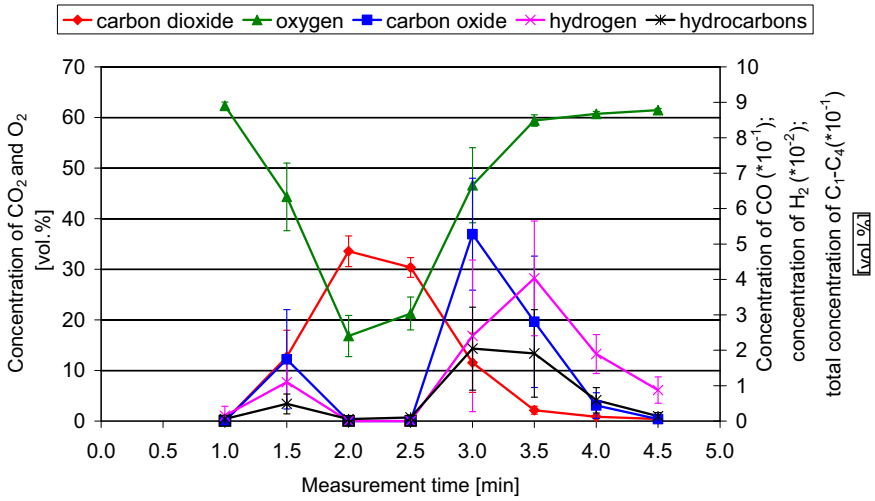

Fig. 5. The course of curves of CO_2, O_2, CO, H_2 concentrations and the course of curve of total concentration of hydrocarbons C_1–C_4 (C) in the post-reaction gas during the 25 g PE samples utilization (data from the gas chromatography).

Table 4
Concentrations of CO_2, O_2, CO, H_2 total concentration of hydrocarbons C_1–C_4 (C) in the post-reaction gas during the 25 g PE samples utilization (data from the gas chromatography).

Measurement time [min]	CO_2 [vol.%]	O_2 [vol.%]	CO (10^{-1} [vol.%]	H2 (10-2 [vol.%]	C_1–C^4 (10^{-1} [vol.%]
1	0,018	62,3	0	0,153	0,060
1,5	12,7	44,3	1,74	1,10	0,486
2	33,6	16,8	0	0	0,055
2,5	30,4	21,3	0	0	0,101
3	11,5	46,6	5,27	2,41	2,04
3,5	2,20	59,4	2,80	4,03	1,91
4	0,860	60,7	0,441	1,894	0,587
4,5	0,444	61,5	0,056	0,877	0,140

the pyrolytic gas flowing out of the pyrolytic reactor (Figs. 3 and 5). The CO concentration reached two maxima. First maximum was when the momentary CO_2 concentration increased with the pyrolysis progress and when the concentration of the hydrocarbons in the pyrolytic gas also increased. Second maximum of CO concentration was when the CO_2 concentration decrease with the ending of the pyrolysis process and the decrease of the hydrocarbon's concentration in the pyrolytic gas. As a result, two peaks of CO concentration were observed. The maximum CO concentration for the measured time of 1.5 min was lower than the maximum CO concentration for the measured time equaling to 3.0 min. Temperature of gas in the plasma reactor corresponding to the first of the peaks was equal to about 450 °C, while the other maximum corresponded to temperature equal to 370 °C (Fig. 4). In contrast, the difference in discharge power values corresponding to the two maxima was only about 0.65 kW (Fig. 4). Thus, the value of concentration of CO was related to the gas temperature obtained in the plasma reactor, and hence the concentration of oxidized hydrocarbons contained in the

pyrolytic gas. If the value of CO concentration in the post-reaction gas is a measure of the efficiency of the oxidation process of the pyrolytic gas, then the oxidation is more effective when the gas temperature obtained in the plasma reactor is higher.

H_2 was not observed at the time of the most efficient oxidation of the pyrolytic gas. The momentary H_2 concentration reached two maxima (Fig. 5). Their heights corresponded to the gas temperature in the plasma reactor. As for CO, the higher the temperature, the lower the concentration of H_2 in the post-reaction gas.

The concentration of aliphatic hydrocarbons C_1–C_4 was analyzed not only in the pyrolytic gas, but also in the post-reaction gas. Total concentration of these hydrocarbons (C) varied during the experiment in a similar way to the concentration of CO and H_2. Total concentration of these hydrocarbons was equal to 0.06% by volume. (Fig. 5).

A carbon balance calculation was performed in order to discover whether PE was decomposed completely to gaseous products in the pyrolytic reactor and whether these products were completely oxidized in the plasma reactor. The number of carbon moles contained in PE sample was compared with the number of carbon moles contained in the components of the post-reaction gas. The following equations were used:

$$n_{PE} = n_{CO_2} = n_{CO} + n_{C_MH_n} \quad (1)$$

$$n_{PE} = m_P / M_{CH_2} \quad (2)$$

where:

n_{PE}—number of carbon moles contained in the sample of PE;

n_{CO_2} , n_{CO} , $n_{C_mH_n}$ —number of carbon moles contained in CO_2, CO and aliphatic hydrocarbons contained in the post-reaction gas of oxidation of hydrocarbons formed during the thermal decomposition of PE;

m_P—PE sample weight [g];

M_P—CH_2 molar mass [g/mol];

The number of carbon moles contained in CO_2, CO and aliphatic hydrocarbons (C_mH_n) (n_i) was calculated with a use of the equation:

$$n_i = m_i \frac{1}{22,4 \times 10^2} \int_0^t c_i V dt \quad (3)$$

where:

m_i—the number of carbon atoms in the molecules of CO_2, CO and C_mH_n;

c_i—concentration of CO_2, CO and C_mH_n in the post-reaction gas [vol.%];

V—flow rate of the post-reaction gas [Nl/min];

t—measurement time [min].

For the calculations the mean values of the obtained parameters of the waste utilization process were used, for these experiments whose parameters are shown in Table 3. It turned out that 99.74% of carbon moles contained in the PE samples were detected in the post-reaction gas (standard deviation 1.883). Thus, the PE samples were practically fully pyrolyzed into hydrocarbons, which were completely oxidized in the plasma reactor.

3.2. Utilization of EW

The use of the model waste, which was the poliethylene (PE), in the experiments, enabled the quantitative verification of the operation of each particular module of MLDWU. The next stage of the research was to verify whether the device would operate properly during the utilization of the real waste, which was the electronic waste (EW).

As a result of the pyrolysis of EW samples, a solid residue was accumulated inside the pyrolytic reactor, since EW contained only 40.38% wt. of combustible parts, which contained 80.21% wt. volatiles. As a result of the pyrolysis, the combustible part content in the solid residue decreased nearly four times and the volatile's content decreased almost seven times in comparison to the raw EW. The elemental composition of the solid residue showed that it consisted mainly of carbon and oxygen. There was no hydrogen present (Table 2).

During the pyrolysis process not only the gaseous products were formed, but also liquid products. Drops of liquid were introduced also into the plasma reactor with argon and the pyrolytic gas. Sometimes the liquid products of pyrolysis significantly disturbed the introduction of the pyrolytic gas into the plasma reactor; therefore the module of pyrolytic reactor was additionally equipped with a system for collecting these liquid products. Thereby, they were introduced into the plasma reactor in smaller amounts.

In the plasma reactor, both gaseous and liquid EW pyrolysis products were oxidized. The course of the curves describing the changes in concentration of the components of the post-reaction gas with the measurement time was more complicated than the course of the similar curves for PE samples (Figs. 5 and 6, Table 5). Two maxima for CO_2 concentration and two minima for O_2 con-

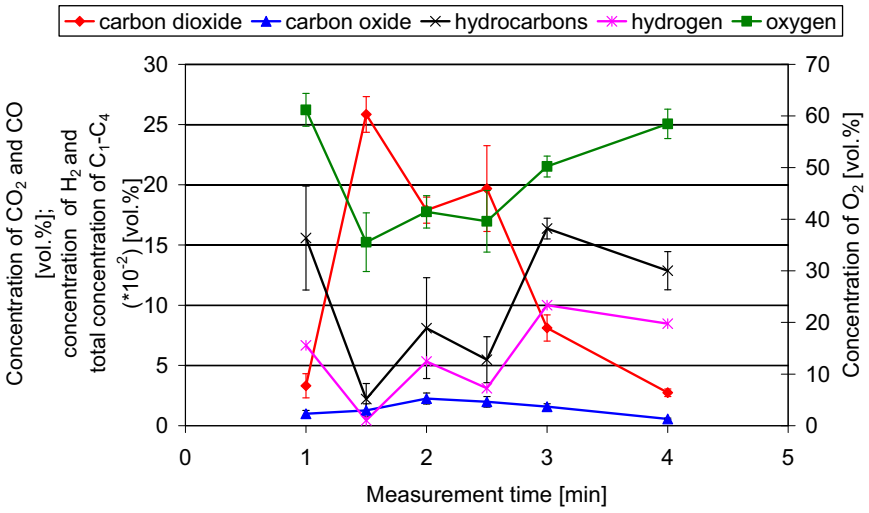

Fig. 6. The course of curves of CO_2, O_2, CO, H_2 concentrations and the course of curve of total concentration of hydrocarbons C_1–C_4 (C) in the post-reaction gas during the 150 g EW samples utilization (data from the gas chromatography).

Table 5
Concentrations of CO_2, O_2, CO, H_2 and total concentration of hydrocarbons C_1–C_4 (C) in the post-reaction gas during the 150 g EW samples utilization (data from the gas chromatography).

Measurement time [min]	CO_2 [vol.%]	O_2 [vol.%]	CO [vol.%]	H_2 (10^{-2} [vol.%]	C_1–C_4 (10^{-2} [vol.%]
1	3,32	61,2	0,997	6,67	15,6
1,5	25,8	35,5	1,28	0,436	2,21
2	17,9	41,4	2,25	5,33	8,09
2,5	19,7	39,6	1,98	3,11	5,47
3	8,10	50,2	1,57	10,0	16,4
4	2,74	58,5	0,56	8,46	12,9

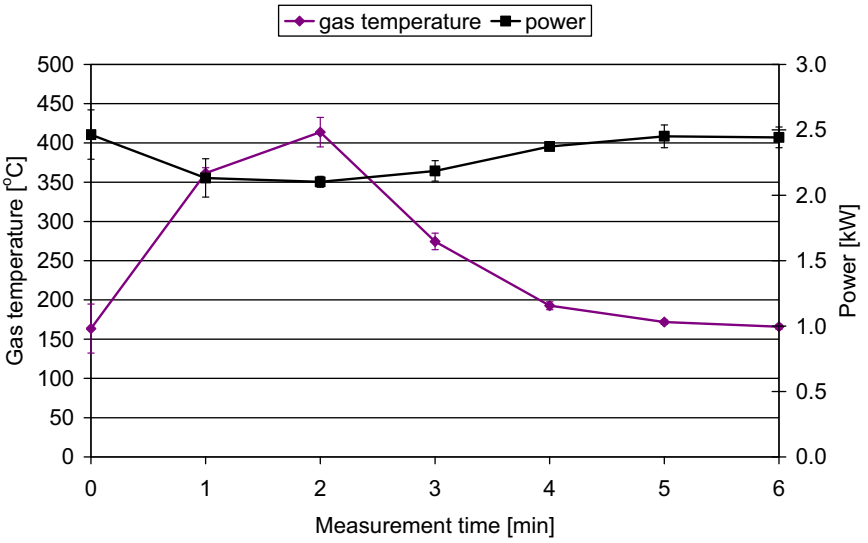

Fig. 7. The course of curve of the gas temperature at the end of the plasma reactor and the course of curve of power supplied to the plasma reactor during EW samples utilization.

centration were observed. This was a result of the fact that EW consisted of two main groups of components differing in thermal properties. After comparing the course of the concentration curves of the individual components of the post-reaction gas at the measured time for each of the EW components separately with changes of the concentration of components of the post-reaction gas of PE utilization, it turned out that they were similar. The values of the highest CO concentration in the post-reaction gas obtained during the oxidation of the EW pyrolysis products were approximately four times higher than those obtained during the oxidation of the products of PE pyrolysis. Maximum H_2 concentration and maximum total concentration of hydrocarbons in the post-reaction gas were also significantly higher than those obtained during the oxidation of the pyrolytic gas from the PE pyrolysis. The efficiency of the oxidation of products after EW pyrolysis was lower than the efficiency of the oxidation of products after PE samples pyrolysis. It can be assumed that this was the result of above four times lower calorific value of EW in comparison to the calorific value of PE. As a result, the maximum gas temperature in the plasma reactor during the oxidation of EW pyrolysis products was about 150 °C lower in comparison to the maximum temperature observed during the oxidation of PE pyrolysis products (Figs. 4 and 7). The power of the plasma reactor was also the cause of the observed temperature decrease. As was mentioned previously in the article, no concentrations of CO and H_2 corresponding to the maximum of CO_2 concentration were observed during the oxidation of PE pyrolysis products. In contrast, after the oxidation of EW pyrolysis products, concentrations of CO amounted to 1.28% vol. and 1.98% vol. and concentrations of H_2 amounted to 0.44% vol. and 3.11% vol. H_2, respectively for the first and second maximum of CO_2 concentration. Similarly, the gas after PE utilization contained only 0.06% vol. of aliphatic hydrocarbons, while after the EW utilization the concentrations of aliphatic hydrocarbons amounted to 2.21% vol. and 2.48% vol. for the first and the second maximum of CO_2 concentration, respectively. The mentioned concentrations of CO and H_2 and a total hydrocarbon concentration confirmed the conclusions drawn on the basis of the results relating to the PE as the model waste and on the relationship between the temperature in the plasma reactor and the efficiency of the oxidation of the pyrolysis products (Figs. 4–7).

4. Conclusions

1 The modular large scale laboratory device for the waste utilization with a use of the pyrolytic-plasma method is an effective tool for studying the process of waste utilization, including those containing chlorine in the elemental composition.
2 The plasma reactor operating on the gliding discharge principle used in the modular device for the waste utilization is an effective tool for the process of oxidation of the pyrolysis products.
3 It can be assumed that the most preferred solution is to use a continuous process of introducing the waste into the pyrolytic reactor, in order to keep constant and as high as possible concentration of hydrocarbons in the pyrolytic gas. Then, high gas temperature is maintained in the plasma reactor, which ensures high efficiency of the oxidation process.
4 Higher calorific value of the waste (similar to that of polyethylene) causes the oxidation of the hydrocarbons, contained in the pyrolytic gas, to be more efficient.
5 It is the most preferred to select the conditions of the waste pyrolysis that allow the formation of mainly gases and vapors.

6 The method of the waste utilization with a use of the modular large scale laboratory device enables recover the desired components of the solid residue after pyrolysis.
7 It can be assumed that the effective oxidation of the waste with a low calorific value requires the application of higher power values in the plasma reactor than those used in the described experiments.

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